Europium complex as a highly efficient red emitter in electroluminescent devices

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Several devices using a europium complex $Eu(TTA)_3(DPPz)$(TTA=2-thenoyltrifluoroacetonate, DPPz=dipyrido[3,2-a:2′,3′-c]phenazine) as dopant emitter were fabricated. The performances of these devices are among the best reported for devices incorporating a europium complex as a red emitter. One such device with structure TPD (50 nm)/Eu:CBP (4.5%, 30 nm)/BCP (30 nm)/Alq (25 nm) exhibits an external quantum efficiency 2.1%, current efficiency 4.4 cd/A, power efficiency 2.1 lm/W, and brightness 1670 cd/m^2. © *2002 American Institute of Physics.*
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Highly efficient electroluminescent materials incorporating complexes of heavy metals are much sought. In addition to well known porphyrin platinum and 2-phenylpyridine derivatives of iridium complexes,[1–5] rare-earth complexes are expected to show high luminance efficiency with sharp emission bands involving electrons associated with inner f orbitals of the central rare-earth metal ions.[6] Emission from these metal complexes originates from excitation of ligands followed by intersystem crossing from the singlet state S_1 to the ligand triplet state T_1; intramolecular transfer of energy from the lowest excited triplet state of the ligand then leads to excitation of the central rare-earth metal ion.[7]

Of rare-earth complexes studied, europium complexes appear most attractive in view of the high photoluminescent (PL) efficiency and the red-emission ability that are widely exploited in full-color displays.[8] Despite efforts of several groups to apply europium complexes as red emitters in electroluminescent devices, only limited success has been achieved.[8–12] Most europium complexes used in electroluminescent devices absorb UV light and emit red light at ~612 nm due to the unique mechanism of excitation. Moreover, europium complexes generally have low-lying highest unoccupied molecular orbital levels because the oxidative state of the europium ion is relatively high. These properties have made it difficult to choose proper materials to fabricate devices. By using BCP or the europium complex itself as the hole blocker in a Eu-based device, several groups have successfully produced saturated red light. Hong and co-workers reported a highly efficient electroluminescent device with external quantum efficiency 4.6% involving a mixed $Eu(DBM)_3$bath and TPD layer, but that efficiency was attainable at current density only 0.01 mA/cm^2.[12] Devices based on $Eu(TTA)_3(phen)$ in CBP using BCP as a hole blocker produce red emission at ~612 nm.[5,10] A few papers on various europium complexes as red emitters have also appeared.[13–19] Although many europium complexes are synthesized and known to give strong luminescence, only several complexes have served in the fabrication of an electroluminescent device. In all cases, the current density and the brightness of these devices were much smaller than those based on pure organic compounds. There appears to exist no device based on a europium complex that can emit saturated red light with brightness greater than 1000 cd/m^2. The design of new ligands and the synthesis of new europium complexes to improve device efficiency are therefore crucial for practical application. In this letter, we report the synthesis of an europium complex $Eu(TTA)_3(DPPz)$, in which TTA is 2-thenoyltrifluoroacetonate and DPPz is dipyrido[3,2-a:2′,3′-c]phenazine (Fig. 1), and the use of this complex as a red emitter in electroluminescent devices. Such devices with this complex as a dopant show brightness greater than those reported based on other known europium complexes.

The DPPz ligand is conveniently prepared in a two-step process. 1,10-Phenanthroline is first oxidized to a dione that then reacts with 1,2-phenylenediamine to afford DPPz.[20] The europium complex was synthesized from $EuCl_3$, 2-thenoyltrifluoroacetone, DPPz and triethylamine in ethanol at 50 °C for 3 h;[21] this complex was purified on sublimation (220 °C, 5×10^{-5} Torr) before device fabrication. Absorption and emission spectra in CBP of this europium complex $Eu(TTA)_3(DPPz)$ are presented in Fig. 2(a).

Electroluminescent devices based on the europium complex were fabricated through vacuum deposition of the materials onto clean glass precoated with a layer of indium tin oxide (sheet resistance 25 ohm/square) at 10^{-6} Torr. The rate of deposition of each organic compound was 1–3 Å s^{-1} and for the europium complex was 0.05–0.1 Å s^{-1}. The cathode was formed through coevaporation of Mg and Ag

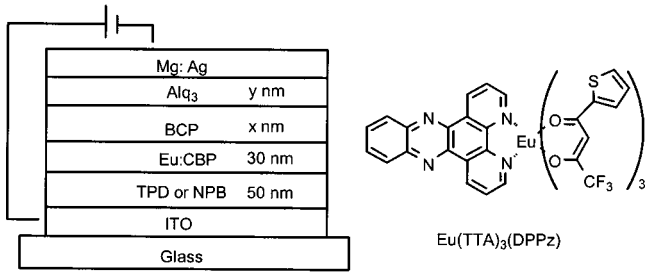

FIG. 1. General structure of the device and molecular structure of $Eu(TTA)_3(DPPz)$.

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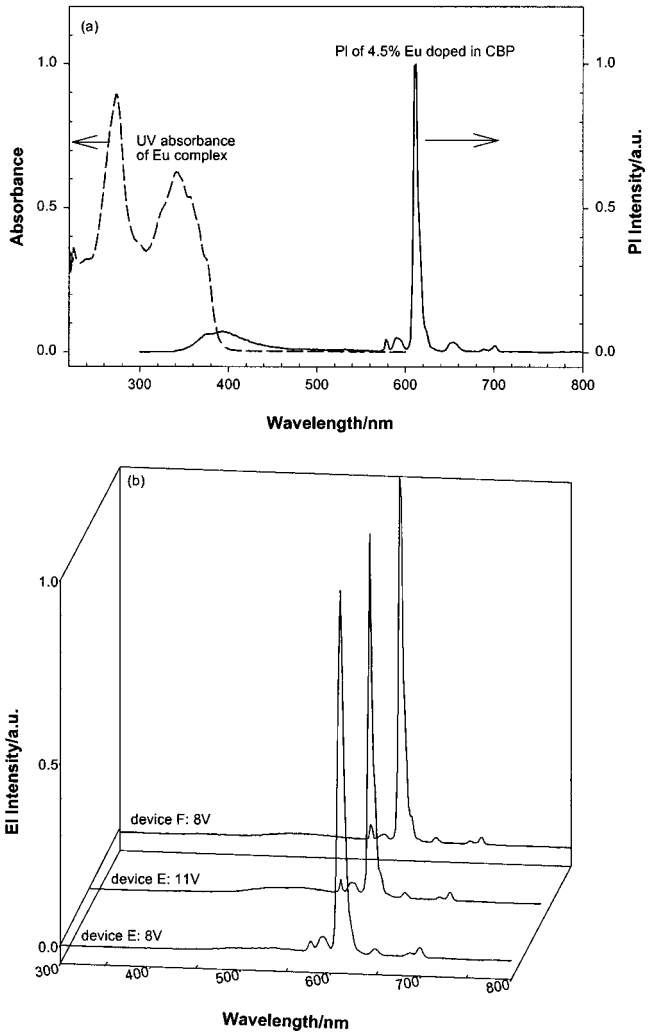

FIG. 2. (a) PL spectrum of a thin film (40 nm) of CBP doped with $Eu(TTA)_3(DPPz)$ (4.5%), and UV absorption spectrum of $Eu(TTA)_3(DPPz)$ (CH_2Cl_2 solution, 10^{-5}M). (b) EL spectra of device **E** [TPD(50 nm)/$Eu(TTA)_3(DPPz)$:CBP (4.5%, 30 nm)/BCP (30 nm)/Alq (25 nm)] at 8 V and 11 V, and device **F** [NPB (50 nm)/$Eu(TTA)_3(DPPz)$:CBP (2%, 30 nm)/BCP (30 nm)/Alq (25 nm)] at 8 V.

with Mg:Ag ratio 10:1 and total thickness 55 nm, followed by vacuum deposition of Ag (100 nm). Rates of codeposition of Mg and Ag were 6 and 0.6 Å s^{-1}, respectively; the rate of deposition of Ag was 3 Å s^{-1}. The emitting diode has an effective area 9.00 mm^2. Current, voltage, and light intensity were measured simultaneously using a source meter (Keithley 2400) and an optical meter (Newport 1835-C) equipped with a silicon photodiode (Newport 818-ST). PL and electroluminescent (EL) spectra were measured on a fluorimeter (Hitachi F-4500), whereas UV-visible absorption spectra were recorded with a spectrophotometer (Hitachi U-3300). All chemicals used for EL devices were purified through sublimation in a vacuum.

Figure 1 shows the general structure of the device and the molecular structure of $Eu(TTA)_3(DPPz)$. TPD (4,4′-bis[*N*-(*p*-tolyl)-*N*-phenyl-amino]biphenyl) or NPB (4,4-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl) served as the hole transporter, whereas Alq_3 (tris[8-hydroxyquinoline]) was the electron transporter. Above the layer of hole transporter was a layer of CBP (4,4′-*N*,*N*′-dicarbazole-biphenyl) doped with $Eu(TTA)_3(DPPz)$ at 1%–8%. Layers of BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) to serve as a hole blocker and of Alq as an electron transporter were subsequently deposited. Several devices with structures similar to that shown in Fig. 1 with $Eu(TTA)_3(DPPz)$ as dopant emitter were fabricated; key characteristics of these devices are listed in Table I.

TABLE I. Device performance of $Eu(TTA)_3(DPPz)$-based OLEDs.[a]

Device[b]	J (mA/cm^2, V)	η_{ext} (%)	L (cd/m^2)	η_c (cd/A)	η_p (lm/W)
A	1, ⋯	⋯	⋯	⋯	⋯
	10, 8.6	1.47	267	2.67	0.98
	100, 11.5	0.70	1272	1.28	0.35
B	1, ⋯	⋯	⋯	⋯	⋯
	10, 8.2	1.13	193	1.94	0.75
	100, 10.7	0.53	893	0.90	0.27
C	1, 5.5	0.40	8	0.82	0.47
	10, 8.7	1.17	235	2.38	0.87
	100, 11.6	0.46	919	0.93	0.25
D	1, ⋯	⋯	⋯	⋯	⋯
	10, 8.2	1.08	221	2.24	0.87
	100, 10.8	0.45	925	0.94	0.27
E	1, 6.4	1.98	43	4.25	2.09
	10, 8.4	1.31	279	2.67	1.04
	100, 11.3	0.49	1036	1.01	0.29
F	1, 7.3	1.29	26	2.56	1.10
	10, 9.9	1.54	303	3.03	0.97
	100, 12.5	0.66	1303	1.30	0.33
G	1, 6.6	1.58	34	3.34	1.59
	10, 8.6	1.10	232	2.31	0.85
	100, 11.2	0.43	921	0.92	0.26

[a]External quantum efficiency (η_{ext}), luminance (L), current efficiency (η_c), and power efficiency (η_p) are given as functions of current density.
[b]Device **A**: TPD (50 nm)/Eu:CBP (1.4%, 30 nm)/BCP (20 nm)/Alq (35 nm), device **B**: TPD (50 nm)/Eu:CBP (2.9%, 30 nm)/BCP (20 nm)/Alq (35 nm), device **C**: TPD (50 nm)/Eu:CBP (5.3%, 30 nm)/BCP (20 nm)/Alq (35 nm), device **D**: TPD (50 nm)/Eu:CBP (7.5%, 30 nm)/BCP (20 nm)/Alq (35 nm), device **E**: TPD (50 nm)/Eu:CBP (4.5%, 30 nm)/BCP (30 nm)/Alq (25 nm), device **F**: NPB (50 nm)/Eu:CBP (2.0%, 30 nm)/BCP (30 nm)/Alq (25 nm), and device **G**: NPB (50 nm)/Eu:CBP (4.5%, 30nm)/BCP (30 nm)/Alq (25 nm).

Device **A** using TPD as hole transporter and $Eu(TTA)_3(DPPz)$ (1.4%) in the CBP layer shows characteristic red emission of Eu^{+3} at 610 nm, an emission line at ~400 nm and trace emission at 520 nm. The feature at ~400 nm likely arises from TPD and CBP, whereas emission at 520 nm is from Alq_3. Despite these features that were present at high voltage, the device had an impressive external quantum efficiency 1.5%, current efficiency 2.7 cd/A at 8.5 V, and current density 9.2 mA/cm^2. At this applied potential, the contribution from emission at 400 nm is small. Inspired by the performance of device **A**, we made devices by adjusting the concentration of $Eu(TTA)_3(DPPz)$ in the CBP layer to improve the efficiency and to diminish the contribution from features at 400 and 520 nm. Devices **B**–**D** had concentrations 2.9%, 5.3%, and 7.5%, respectively, of the europium complex. The emission at 400 nm became weak for device **B**. Further increased concentration of $Eu(TTA)_3(DPPz)$ to 5.3% and 7.5% in the CBP layer efficiently quenched the 400 nm emission as shown in devices **C** and **D**. Devices **B**–**D** had maximum brightness more than 1500 cd/m^2; external quantum efficiency between 1.2% and 1.4%, current efficiency in a range 2.0–2.8 cd/A and power

TABLE II. Summary of Eu-based OLEDs in literature.

Emitter layer	(η_{ext}, J) (%, mA/cm^2)	(L, V) (cd/m^2, V)	(η_p, J) (lm/W, mA/cm^2)	Reference
Eu(TTA)$_3$(DPPz)/CBP (4.5%)	2.1, 1.23	1670, 13.6	2.1, 1.23	This work
Eu(DBM)$_3$(phen)/PBD (1/3)	···	460, 16.0	···	6
Eu(DBM)$_3$(phen)	···	50, 15.0	···	8
Eu(DBM)$_3$(bath)/TPD (3/1)	1.0, 0.6	820, 18.0	1.0, 0.6	9
Eu(DBM)$_3$(bath)/TPD (2/1)	4.6, 0.01	···	···	12
Eu(DBM)$_3$(bath)	···	400, 15.0	···	15
Eu(TTA)$_3$(phen)/CBP (1%)	1.4, 0.4	505, 12.0	···	10
Eu(DCNP)(DBM)$_2$(phen)/PBD (10%)	3.5, 0.17	924, ···	2.0, 0.17	11

efficiency in a range 0.8–1.2 lm/W. Device **E** was fabricated on adjusting the thicknesses of BCP and Alq layers. A comparison of devices **C** and **E** indicates that increasing the thickness of the BCP layer and decreasing that of Alq yielded increases device efficiency. The greatest external quantum efficiency 2.1%, current efficiency 4.4 cd/A, power efficiency 2.1 lm/W, and brightness 1670 cd/m^2 were obtained from device **E** with BCP and Alq layers 30 and 25 nm thick, respectively. The performances of these devices at current densities 1, 10, and 100 mA/cm^2 are shown in Table I. The performances of these devices are among the best reported for devices incorporating a europium complex as a red emitter. For comparison, a summary of the performance of Eu-based organic light-emitting diodes (OLEDs) in literature is listed in Table II.

In addition to TPD, we tested the efficiency of NPB as a hole transporter for devices based on Eu(TTA)$_3$(DPPz). Two devices **F** and **G** with Eu(TTA)$_3$(DPPz) concentrations 2.0% and 4.5% in CBP were thus fabricated. A strong red emission at 612 nm for device **F** with essentially no emission at 400 and 520 nm was observed [Fig. 2(b)]. The external quantum efficiency, current efficiency and power efficiency are listed in Table I. The maximum brightness of this device exceeds 2000 cd/m^2. For all these devices, onset of a weak emission feature at ~520 nm, likely due to the emission of Alq, occurs at applied potential ~14 V. At current densities shown in Table I, the intensity of this emission is much less than that of the line at 612 nm for devices **B**–**G**; saturated red light is emitted from these devices.

As revealed in Fig. 2(a), the PL spectrum of a thin film of Eu(TTA)$_3$(DPPz) (4.5% in CBP) contains significant emission from CBP centered at 390 nm in addition to the characteristic line of Eu^{+3} at 612 nm. The observed spectra differ appreciably from EL spectra of devices **C**, **E**, and **G** in which the CBP layer also consists of ~5% Eu(TTA)$_3$(DPPz). EL spectra of these devices contain essentially no emission at 390 nm. These results conform to a carrier-trapping mechanism suggested for EL of devices based on europium complexes.[10] For the present EL, another possible mechanism involving solo Förster energy transfer from host CBP to dopant Eu(TTA)$_3$(DPPz) appears unlikely in view of the observed difference of PL and EL spectra presented in Fig. 2, but an involvement of both carrier trapping and Förster energy transfer can not be excluded.

In conclusion, we have demonstrated that EL devices based on Eu(TTA)$_3$(DPPz) emit red light at 612 nm with great brightness, external quantum efficiency, current efficiency, and power efficiency. These values are among the best reported for devices with europium complexes as emitters. The present results indicate that the design of ligands is crucial to enhance the performance of EL devices based on rare-earth metal complexes. The methods of synthesis of DPPz and Eu(TTA)$_3$(DPPz) are applicable to preparation of phenanthroline derivatives and europium complexes; investigation in this direction is in progress.

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[1] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).
[2] D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **74**, 442 (1999).
[3] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **75**, 4 (1999).
[4] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, and M. E. Thompson, J. Am. Chem. Soc. **123**, 4304 (2001).
[5] C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, and R. C. Kwong, Appl. Phys. Lett. **78**, 1622 (2001).
[6] J. Kido, H. Hayase, K. Hongawa, K. Nagai, and K. Okuyama, Appl. Phys. Lett. **65**, 2124 (1994).
[7] O. L. Malta, H. F. Brito, J. F. S. Menezes, F. R. Goncalves e Silva, C. de Mello Donega, and S. Alves, Jr., Chem. Phys. Lett. **282**, 233 (1998).
[8] H. Heil, J. Steiger, R. Schmechel, and H. von Seggern, J. Appl. Phys. **90**, 5357 (2001).
[9] C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, X. Y. Liu, W. L. Li, J. B. Peng, J. Q. Yu, C. S. Lee, and S. T. Lee, Appl. Phys. Lett. **76**, 67 (2000).
[10] C. Adachi, M. A. Baldo, and S. R. Forrest, J. Appl. Phys. **87**, 8049 (2000).
[11] M. Noto, K. Irie, and M. Era, Chem. Lett. **2001**, 320 (2001).
[12] Z. Hong, C. Liang, R. Li, W. Li, D. Zhao, D. Fan, D. Wang, B. Chu, F. Zang, L. S. Hong, and S. T. Lee, Adv. Mater. **13**, 1241 (2001).
[13] R. A. Campos, I. P. Kovalev, Y. Guo, N. Wakili, and T. Skotheim, J. Appl. Phys. **80**, 7144 (1996).
[14] L. Liu, W. Li, Z. Hong, J. Peng, X. Liu, C. Liang, Z. Liu, J. Yu, and D. Zhao, Synth. Met. **91**, 267 (1997).
[15] C. J. Liang, Z. R. Hong, X. Y. Liu, D. X. Zhao, D. Zhao, W. L. Li, J. B. Peng, J. Q. Yu, C. S. Lee, and S. T. Lee, Thin Solid Films **359**, 14 (2000).
[16] W. Zhu, Q. Jiang, Z. Lu, X. Wei, M. Xie, D. Zou, and T. Tsutsui, Synth. Met. **111**, 445 (2000).
[17] W. Hu, M. Matsumura, M. Wang, and L. Jin, Appl. Phys. Lett. **77**, 4271 (2000).
[18] G. Yu, Y. Liu, X. Wu, and D. Zhu, Chem. Mater. **12**, 2537 (2000).
[19] L. Huang, K. Z. Wang, C. H. Huang, F. Y. Li, and Y. Y. Huang, J. Mater. Chem. **11**, 790 (2001).
[20] A. M. S. Garas and R. S. Vagg, J. Heterocycl. Chem. **37**, 151 (2000).
[21] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Laris, J. Am. Chem. Soc. **86**, 5117 (1964).